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Controlling the Quality of Clinker.

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In the manufacture of cement the element most left to chance or to human judgment is the quality of the clinker. Considerable efforts are usually made to maintain a certain chemical composition, or if this cannot be done the relative proportions are adjusted so that the result is reasonably satisfactory. For example, if the percentage of silica in the raw materials is variable, either the percentage of silica is kept reasonably constant in the clinker by adding a more siliceous or a more aluminous material from time to time, or the percentage of lime in the clinker is varied as the percentage of silica varies, so that the final result is a suitable composition. The fineness of the slurry, the slurry moisture, and so on, are controlled, and the finished cements are tested in order to obtain the best and most uniform product. All these controls are maintained on a quantitative basis, but for controlling the clinker quality the obvious method of measuring the clinkering temperature and maintaining this constant has been tried again and again, with unsatisfactory results on account of the difficulty of obtaining accurate or comparative figures in the rotary kiln.

The quality of the clinker is therefore usually controlled as far as possible by its appearance in the kiln, its hardness, its appearance on fracture, its appearance on leaving the cooler, its size, etc. A good many years ago, however, a more quantitative method was introduced, I believe by Mr. Pontoppidan, of Copenhagen. The method was to take a sample of clinker from the kiln and grade it to a uniform size by sieving through two screens, the fraction retained between the two being tested for weight per litre. This test appears to have been introduced when the manufacture of rapid-hardening cement became common and a closer control of the quality of the clinker was necessary. The test is carried out in the same way as the test of cement for weight per litre, the

burner being provided with the necessary sieves, a measuring flask, funnel, and pair of scales. The burner makes the test, say, every two hours. To anyone who has not used this check it may not seem very helpful, but I think most people who have used it for a few months would be sorry to give it up. There is a relation between the weight per litre and the hardness of burning, and the relationship is fairly uniform. Very occasionally quite anomalous results are found ; the kiln appears to be quite hot, but very light weights occur. This only seems to happen if the kiln has been upset by an involuntary stop. Apart from this the burner can be given a figure of weight per litre to aim at, and the figures he actually obtains give some guide to the clinker quality. To a considerable extent the check is quantitative.

After using the method for some years, largely because it tells the burner something about what he is doing, at this factory we had come to the conclusion that it is very useful. We find that check tests agree reasonably well, and that on the whole we have improved the quality of clinker since using the test, producing a harder burned and more uniform clinker. The burners also seem to obtain better control of the kiln, probably because they see very often the effect of their manipulations of coal and damper on the weight of the clinker.

A recent article in *Zement* which cast doubts on the use of the test, drew more attention to it here. The conclusion the writer in *Zement* came to, namely, that the results are very erratic, is certainly incorrect as far as this factory is concerned, except on some rare occasions when the kiln has been upset and the results have been completely useless. Unfortunately, we have never been able to reproduce this artificially, and have never been able to suggest a cause for it. It happens so rarely, however, that it can be neglected. That writer's incredulity, however, suggested that the advantage of the test could be increased if more were known about it, and it was therefore arranged that the kiln should be heated as far as reasonably possible and then allowed to cool down ; whilst in the process of cooling corresponding samples were taken and tested.

The results of the first test were not completely satisfactory, as insufficient samples were taken and the gaps between the samples were too great. Four samples were taken, and these were ground in an experimental mill to approximately the same flour content for each sample. From each clinker sample two samples of cement were prepared, one of which was supposed to correspond to ordinary cement and the other one to rapid-hardening cement. It would have been better if both samples had been ground more finely, say, to 64 per cent. and 82 per cent. flour content respectively, rather than the 60 per cent. and 75 per cent. aimed at. The flour was determined by a Baird & Fitch flourometer.

As mentioned, the kiln was heated as hot as reasonably possible without badly balling the clinker, and thirty minutes afterwards the first sample was taken at the coolers. This corresponds to the time necessary for the clinker to travel from the clinkering zone to the cooler outlet. As soon as the kiln was hot the coal feed was reduced, and samples were taken every four minutes as the kiln cooled. The separate samples were then ground in an experimental ball

mill, with the same amount of gypsum, to as nearly as possible the same residue, and the resulting cements tested with the results given in Table I.

TABLE I.

Sample No.	1	2	3	4
Clinker weight (kg. per litre)	1·36	1·40	1·51	1·60
Residue on 170² sieve (per cent.)	12·80	12·0	13·2	12·60
Flour content (per cent.)	59·80	60·7	60·4	59·20
3 : 1 tensile test (B.S.S.), lb. per sq. in. :				
3 days	380	481	483	398
7 ,,	425	513	522	471
3 : 1 compression (lb. per sq. in.) :				
1 day	1,599	1,846	1,633	1,760
3 days	3,260	5,207	3,787	3,024
7 ,,	4,970	5,830	5,438	4,260
28 ,,	5,964	6,532	6,343	5,112
28 ,, C.S.	6,579	7,242	6,863	5,964
Concrete strength (approx. 4 : 2 : 1), lb. per sq. in. :				
1 day	227	274	283	256
3 days	956	1,136	1,232	833
7 ,,	1,988	2,035	2,233	1,354
28 ,,	3,171	3,408	3,313	2,556
(Water-cement ratio = 1 by volume.)				
Free lime (per cent.)	0·39	0·07	0·04	0·57
SO_3 (per cent.)	1·70	1·70	1·70	1·70
Le Chatelier expansion test	1 mm.	3 mm.	3 mm.	1 mm.

The samples show that there is a relation between weight per litre and quality of clinker, and as the weight-per-litre tests can be reproduced with an error of about 1 per cent., the test should be useful. It will be noticed that the residue of 12 or 13 per cent. on the 170-mesh sieve is well outside the B.S.S. limits. The flour content of about 60 per cent. corresponds to a residue of about 4 per cent. on cement ground through the factory mill, as the experimental mill generally gives a much higher residue than the factory mill for the same flour. Cements of the same flour content ground through the two mills from the same clinker show approximately the same strengths. The 3 : 1 compression tests were made according to the Australian Standard Specification with the Boehme hammer (150 blows) and British standard sand.

The interesting points about the figures are :

(*a*) The hardest burnt sample does not give the highest concrete strengths.

(*b*) The hardest burnt sample does not show the lowest free lime content.

(*c*) The samples with lowest free lime show the best strengths.

(*d*) There is no relation between Le Chatelier expansion and free lime when the expansion is low.

In other words, there is an optimum burning temperature at which the best clinker is produced, and burning harder or softer than this produces a less satisfactory product.

In Table II are the figures for the more finely ground samples.

TABLE II.

Sample No.	1	2	3	4
Clinker weight (kg. per litre)	1·36	1·40	1·51	1·60
Residue on 170² sieve (per cent.)	7·60	6·60	7·00	7·20
Flour content (per cent.)	73·60	74·60	73·60	74·30
3 : 1 tensile test (B.S.S.), lb. per sq. in. :				
3 days	513	510	556	520
7 ,,	566	627	619	570
3 : 1 compression test (Australian standard), lb. per sq. in. :				
1 day	3,353	3,171	3,976	3,962
3 days	5,112	6,039	5,775	5,680
7 ,,	5,917	6,532	6,390	6,650
28 ,,	7,384	7,100	7,384	7,526
28 ,, C.S.	7,526	7,384	7,668	7,715
Concrete strength (approx. 4 : 2 : 1), lb. per sq. in. :				
1 day	819	852	795	682
3 days	1,704	2,309	1,846	1,552
7 ,,	2,566	3,152	3,408	2,698
28 ,,	3,976	4,118	4,260	4,118
(Water-cement ratio = 1 by volume.)				
Free lime (per cent.)	0·39	0·07	0·04	0·57
SO_3 (per cent.)	1·70	1·70	1·70	1·70

TABLE III.

Sample No.	1	2	3
Clinker weight (kg. per litre)	1·10	1·49	1·52
Free lime (per cent.)	4·41	0·56	0·03
COARSELY GROUND.			
Residue on 170² sieve (per cent.)	15·00	14·2	14·2
Flour content (per cent.)	64·30	65·2	64·8
Concrete strength (approx. 4 : 2 : 1), lb. per sq. in. :			
1 day	426	710	370
3 days	1,434	1,628	1,235
7 ,,	2,087	2,414	2,130
28 ,,	3,266	3,408	2,840
(Water-cement ratio = 1 by volume.)			
SO_3 (per cent.)	1·7	1·7	1·7
FINELY GROUND.			
Residue on 170² sieve (per cent.)	7·0	6·8	6·4
,, 325² sieve (per cent.)	19·4	14·3	17·3
Flour (per cent.)	79·6	79·8	80·1
Concrete strength (approx. 4 : 2 : 1), lb. per sq. in. :			
1 day	614	837	672
3 days	1,789	2,158	1,833
7 ,,	2,854	3,114	2,972
28 ,,	3,834	4,118	3,550
(Water-cement ratio = 1 by volume.)			
SO_3 (per cent.)	2·4	2·4	2·4

On the whole these figures bear out the results of the more coarsely ground samples, but not in so marked a way. The clinker analysis of this series was :

SiO_2	22·8 per cent.
Al_2O_3	5·4 ,,
Fe_2O_3	2·8 ,,
CaO	67·2 ,,
MgO	1·3 ,,
SO_3	0·1 ,,

(B.S.S., CaO = 2·77)

These results were sufficiently interesting to warrant further tests, which were made in the same way, with the results given in Table III.

The analysis of this clinker was :

SiO_2	22·0 per cent.
Al_2O_3	5·4 ,,
Fe_2O_3	3·3 ,,
CaO	67·2 ,,
MgO	1·6 ,,
SO_3	0·1 ,,

(B.S.S., CaO = 2·85)

The figures again bear out that there is an optimum burning point. In this case it appears as if the lime content is too high for the silica content, bearing in mind the slurry residue of 12 per cent. which was maintained throughout. The alteration in the silica content was deliberate.

Two further series of tests were made with the percentages of silica, lime, and iron oxide altered with the results given in Table IV :

TABLE IV.

Sample No.	1	2	3	4	5	6
Clinker weight (kg. per litre)	1·37	1·41	1·47	1·50	1·53	1·59
Free lime (per cent.)	0·03	0·36	0·09	0·11	0·14	0·21
COARSELY GROUND.						
Residue on 170² sieve (per cent.) ..	13·0	13·7	13·4	14·0	14·6	14·0
Flour content (per cent.)	65·2	64·9	65·3	65·0	64·5	64·6
Concrete strength (approx. 4 : 2 : 1), lb. per sq. in. :						
1 day	426	643	738	624	596	511
3 days	1,306	1,467	1,562	1,354	1,292	1,079
7 ,, ...	2,130	2,253	2,285	2,172	1,893	1,683
28 ,, ...	3,124	3,455	3,550	3,313	3,152	2,953
(Water-cement ratio = 1 by volume.)						
SO_3 (per cent.)	1·7	1·7	1·7	1·7	1·7	1·7
FINELY GROUND.						
Residue on 170² sieve (per cent.) ..	4·2	4·6	5·0	5·2	4·7	4·3
,, 325² sieve (per cent.) ..	12·6	13·2	13·0	12·8	12·4	13·8
Flour content (per cent.)	80·1	79·4	79·8	80·5	79·4	79·6
Concrete strength (approx. 4 : 2 : 1), lb. per .sq. in. :						
1 day	824	928	994	909	814	796
3 days	2,319	2,452	2,556	2,348	2,144	1,828
7 ,, ...	3,123	3,215	3,294	3,042	2,793	2,518
28 ,, ...	4,118	4,165	4,260	3,976	3,910	3,635
(Water-cement ratio = 1 by volume.)						
SO_3 (per cent.)	2·4	2·4	2·4	2·4	2·4	2·4

The analysis of this clinker was:

SiO_2	22·3 per cent.
Al_2O_3	4·9 ,,
Fe_2O_3	3·5 ,,
CaO	66·8 ,,
MgO	1·6 ,,

(B.S.S., CaO = 2·84)

The lower lime and higher silica contents account for the lower free lime in this sample.* The figures show in a very definite way that the clinker weight, free lime, and strength are very intimately related, which is also shown by the series of tests in Table V:

TABLE V.

Sample No.	1	2	3	4	5
Clinker weight (kg. per litre)	1·35	1·42	1·49	1·52	1·59
Free lime (per cent.)	0·48	0·14	0·07	Trace	0·14
COARSELY GROUND.					
Residue on 170² sieve (per cent.)	13·5	13·6	13·8	13·2	13·0
Flour content (per cent.)	64·3	65·0	64·8	65·1	65·0
Concrete strength (approx. 4 : 2 : 1), lb. per sq. in.:					
1 day	440	568	605	681	540
3 days	1,259	1,372	1,429	1,476	1,353
7 ,,	2,102	2,366	2,442	2,560	2,074
28 ,,	3,266	3,453	3,692	3,711	3,313
(Water-cement ratio = 1 by volume.)					
SO_3 (per cent.)	1·7	1·7	1·7	1·7	1·7
FINELY GROUND.					
Residue on 170² sieve (per cent.)	4·2	4·2	4·0	4·3	4·0
,, 325² sieve (per cent.)	18·6	19·4	18·4	19·0	18·2
Flour content (per cent.)	79·4	79·1	79·2	79·2	79·6
Concrete strength (approx. 4 : 2 : 1), lb. per sq. in.:					
1 day	766	951	966	1,008	824
3 days	2,102	2,111	2,186	2,253	1,988
7 ,,	2,982	3,200	3,294	3,399	2,868
28 ,,	4,118	4,372	4,402	4,544	4,260
(Water-cement ratio = 1 by volume.)					
SO_3 (per cent.)	2·4	2·4	2·4	2·4	2·4

The analysis of the foregoing series is:

SiO_2	22·8 per cent.
Al_2O_3	4·3 ,,
Fe_2O_3	3·5 ,,
CaO	67·2 ,,
MgO	1·5 ,,
SO_3	0·1 ,,

The following are analyses of the sample containing least free lime in each series:

* The B.S.S. CaO ratios are, however, the same or nearly so.

Table No.	III	IV	I	V
SiO_2 (per cent.)	22·0	22·3	22·8	22·8
Al_2O_3 (per cent.)	5·4	4·9	5·4	4·3
Fe_2O_3 (per cent.)	3·3	3·5	2·8	3·5
CaO (per cent.)	67·2	66·8	67·2	67·2
Clinker weight (kg. per litre)	1·49	1·475	1·51	1·525
Free lime (per cent.)	0·56	0·09	0·04	Trace
COARSE SAMPLE.				
Flour content (per cent.)	65·2	65·3	60·4	65·1
28-day concrete (lb. per sq. in.)	3,408	3,550	3,313	3,711
FINE SAMPLE.				
Flour content (per cent.)	79·8	79·8	75·0	79·2
28-day concrete (lb. per sq. in.)	4,118	4,260	4,260	4,544

In each case these samples showed the best results. It appears that the best clinker is the one containing no free lime, which, at any rate with the sort of slurry used at this works, with 12 per cent. residue on the 170²-mesh sieve, is a definitely hard-burnt clinker, but clinkering above this hardness just as much as clinkering below it is deleterious to the quality of the cement. It certainly does appear from the figures that the contention that experience over many years proves the advantage of measuring the weight per litre for a control of clinker quality is correct.

The burning procedure suggested, then, is to keep the clinker composition as uniform as possible, to find out at what weight per litre the clinker has no free lime, and to try to adhere to that clinker weight. The sieves used have square holes with sides of 7 mm. and 4·5 mm. respectively, and it only takes a few minutes to make a determination.

It is hoped these figures will induce those who do not at present use this handy test to experiment with it.

Hydro-Ferrites of Lime

A NEW ferrite of calcium, $3CaO.Fe_2O_3.6H_2O$, is described by Dr. Antoni Eiger in a recent number of *Revue des Materiaux de Construction* (July, 1937). This compound was obtained by the action of colloidal hydrate of iron oxide on a supersaturated solution of lime in water. The author mentions another hydrate of the composition, $4CaO.Fe_2O_3.7H_2O$, discovered by Hoffman. Thus there exist hydro-ferrites of tri- and tetra-calcium, representing an analog to the already known hydro-aluminates of lime.

According to Messrs. Wm. Lerch and R. H. Bogue,

$$4CaO.Al_2O_3.Fe_2O_3 + xH_2O = 3CaO.Al_2O_3.6H_2O + 3CaO.Fe_2O_3.yH_2O.$$

In Dr. Eiger's opinion the hydrolysis of Brownmillerit may proceed as shown in the equation

$$4CaO.Al_2O_3.Fe_2O_3 + xH_2O = 3CaO.Al_2O_3.6H_2O + 2Fe(OH)_3 + Ca(OH)_2 + yH_2O.$$

Inasmuch as the solution is supersaturated in respect to $Ca(OH)_2$, the formation of hydro-ferrite of lime ($nCaO.Fe_2O_3.yH_2O$) is very probable. A further study of calcium-hydro-ferrites may give us a better understanding of the hydrolysis of Brownmillerit, the knowledge of which is still obscure.

A Modern Kiln-Feed Plant.

PREPARATION of the kiln feed at the reconstructed plant of the Universal Atlas Cement Co., at Leeds, near Birmingham, U.S.A., is accomplished with the most modern equipment available to the industry, and no attempt was made to use any part of the old plant. The new work is described in the Cement Mill Edition of "Concrete" for January, 1939, from which the following notes are taken.

Thickeners and Rock Mill.

In the new plant the two thickeners and the rock-grinding mill (*Figs.* 2 and 3) are operated as a unit. The rock mill is equipped with two closed-circuit grinding

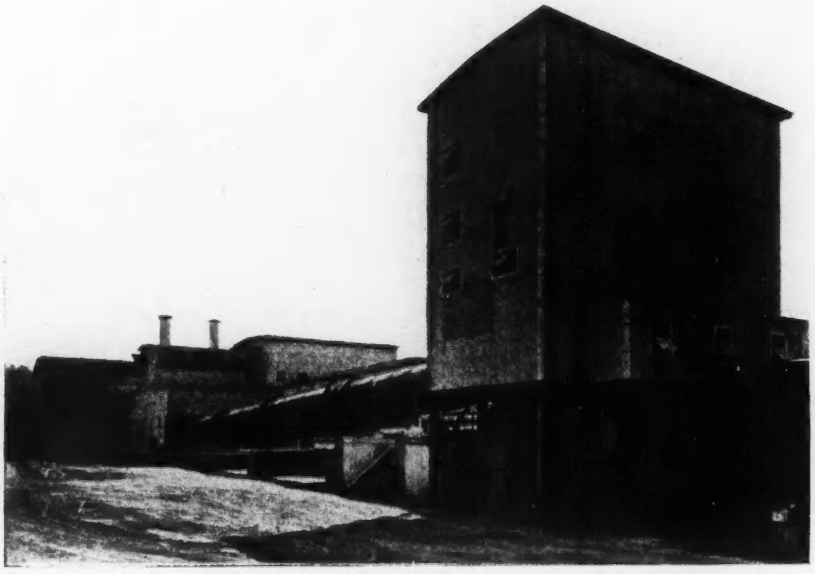

Fig. 1.—Reconstructed Plant: Raw Feed Building on right.

units, and is one of the few mills designed for closed-circuit operation from the start. Each grinding unit consists of a preliminary ball mill 9½ ft. inside diameter and 8 ft. long in closed circuit with a rake classifier. This preliminary ball mill is shown in *Fig.* 2 in the right foreground, and the rake classifier is seen in the centre foreground. The finished product from the rake classifier, which is practically all finer than 20-mesh, is carried by a launder to a 24-ft. bowl classifier. The overflow from the bowl classifier is the finished product that is pumped to the thickeners. The over-size material in the bowl classifier is raked to a sand-wheel (a rotary elevator with buckets on the periphery), and this delivers the over-size to a ball mill of the same dimensions as the preliminary mill. The product of this second ball mill is run back into the bowl classifier. Each of the

ball mills is driven by a 350-h.p., 2,300-volt motor operating at 180 revolutions a minute.

The thickeners are 200 ft. in diameter and each holds about 25,000 barrels of kiln feed. Each is equipped with two re-circulating pumps for blending. One pump delivers part of the thickened slurry to a point about 30 ft. from the centre of the thickener, while the other pump delivers to a point about 60 ft. from the centre. The purpose of having two thickeners is to provide for the necessity of making special cements. One thickener would not provide the required elasticity in operations.

The thickened slurry is pumped to the four kiln-feed storage tanks. Each of these four tanks has enough capacity to hold from five to six hours' supply of

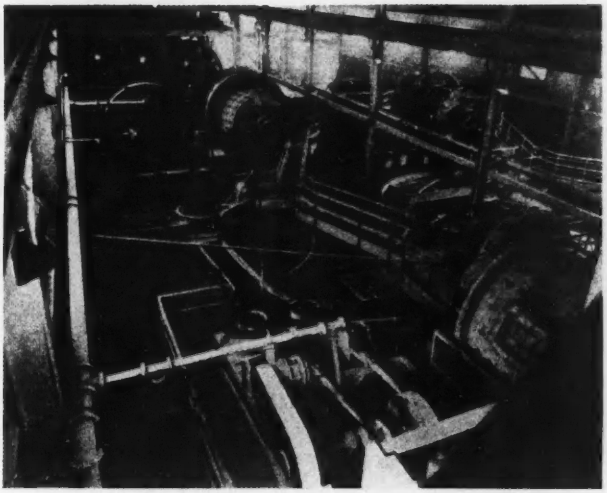

Fig. 2.—Rock Grinding Mill designed for Closed-circuit Operation.

slurry for the two kilns installed in the plant, and is agitated both mechanically and by compressed air.

The Kilns.

The two kilns are each 10 ft. in interior diameter and 300 ft. long. Each kiln has five supports of the 2-roll type, and each is fired by a unit coal mill. An unusual feature of the kilns is the drive, which is a direct-current motor, the speed of which is controlled by a Ward-Leonard system of variable voltage. Each kiln-drive motor has a separate direct-current generator, and the voltage of the current supplied to the kiln motor is controlled by the excitation of the generator. This system provides a wide range of speeds and stable characteristics at any point. Thus the angular velocity of the kilns can be depended upon to be uniform. The speed of the kilns can be varied from 10 to 100 revolutions per hour.

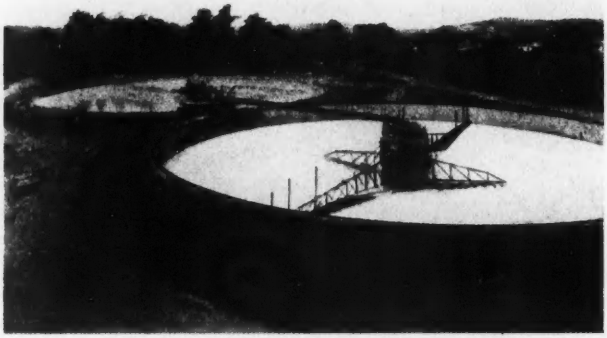

Fig. 3.—200-ft. diameter Slurry Thickeners.

The kilns are oiled from a central circulating system, the surplus oil being returned to the oil house where it is filtered and re-used. Similar provision is made for lubrication of all the grinding mills. Coal is brought to the plant in hopper cars at the far end of the plant (*Fig.* 1) and is dumped into a track hopper, from which it is conveyed to the coal house by a belt conveyor fitted with a magnetic pulley for the removal of tramp iron.

The reconstructed plant has been in operation since March, 1938, and is electrically operated throughout.

Developments During the Year 1938

IN a recent number of " Rock Products," Mr. F. O. Anderegg gives a résumé of some of the more interesting developments in the cement industry during the year 1938, including the following :-

RESISTANCE TO CORROSION.—Ferrari uses an equivalent amount of iron and alumina so as to produce C_4AF only, together with a larger amount of the silicates, to give a cement very resistant to corrosive solutions, including sea water. This may be improved somewhat by incorporating good puzzolanic materials.

CLINKER-WEIGHT AND STRENGTH.—Anselm and Schindler get the apparent unit weight of clinker and claim good correlation with actually determined strengths, clinkers running from 87 to 93 lb. per cu. foot giving best results.

DETERMINATION OF SILICA.—Nagerova and Petrova determine silica in leach water from concretes with the aid of ammonium molybdate in sulphuric acid solution, compared colorimetrically with picric acid solutions.

COMPOSITION.—Sanada offers evidence that magnesia is not taken up by the Portland cement minerals unless insufficient lime is present to form the di-silicate. Jander and Wuhrer, after careful X-ray studies conclude that both di- and tricalcium silicates may take up tricalcium aluminate to the extent of 6 to 7 per cent. at 1,400 deg. C.

ETCHING POLISHED CLINKER.—Tavasci gets interesting microscopic results on etching a polished clinker surface with a 1 per cent. borax solution.

EFFECT OF CALCIUM FLUORIDE.—Eitel finds that calcium fluoride has a valuable mineralising action in forming tri-silicate, but very rapid cooling is required to prevent reversal.

EFFECT OF CALCIUM CHLORIDE AND SODIUM SULPHATE.—Feret observes that calcium chloride and sodium sulphate have little effect on the soundness of cement. The former does accelerate early strength, without having much effect on later strengths. Glaze is useful in securing density so as to reduce opportunity for sulphate attack.

SLAG AND TRASS.—V. Rodt believes that finely ground blastfurnace slag and trass not only act to densify, but also have some specific cementing action in the presence of free lime.

BLENDED CEMENTS.—Nagai believes that high silica blended cements can be made not to have any more shrinkage than standard Portland cements, while showing much better resistance to sulphate solutions.

ALUMINOUS CEMENT.—Nagai has studied aluminous cement for refractory purposes. He finds lime added to improve workability of the concrete also lowers its melting point.

CLINKER BURNING.—Mussgnug, on burning Portland cement clinker from slags in reducing atmosphere, notes a change in colour from dark grey to chocolate brown with reduction in setting times and early strengths. Later, however, the strengths come up to normal.

MASONRY MORTARS.—For masonry mortars, Krüger prefers lime-cement mortars for most units, a straight lime mortar being only regarded as suitable for non-load-bearing walls built of certain clay and slag units. For heavy duty masonry, Portland cement should be the only cementitous material. Well-burned units are also required for load carrying. Drögsler has built a number of masonry piers with German brick and mortars of different strengths. The formula covering the strengths suggested is of the form $S = aB - c/M + D$, where B is the brick strength and M the mortar, while a, c, and D are constants, the latter depending upon the shape of the wall, pier, or panel.

RETEMPERING CONCRETE.—Keil and Gille found that concrete can be stored quite a considerable time beyond the initial set and then reworked, no water being added, without affecting the strength. The mass must have sufficiently good workability to be placed to form a dense concrete. Concrete can also be mixed a very long time without harm, the economic factor limiting the time of mixing. In fact, the long mixing is often very helpful.

TEST FOR FREE LIME.—A valuable test for free lime in Portland cement clinker is described by Schläpfer and Eisenwein, involving the use of clove oil. Highly birefringent (1·59–1·57) rhombic crystals of calcium eugenolate form directly on the CaO indicating its location. Hydroxides of Ca and Mg become yellow, but neither they nor the other constituents of ordinary clinker form the eugenolate crystals.

Coal Consumption of Lime Kilns

VARIATIONS in the coal required to calcine one ton of limestone are dealt with by Mr. N. W. Taylor in the February, 1939, number of *Rock Products*. The first essential, he says, is a tight kiln shell, preferably steel, to seal out all cold air leaks. The next factor is draught. Kilns operated under forced draught usually report more efficient coal consumption, but forced draught has the attendant dangers of overburned lime. An induced draught has less danger of overburning where artificial draught is required. Costs relative to oil-fired or natural-gas fired kilns are not available covering a sufficient period of time or a wide enough range of conditions to give any authentic comparative figures.

The results obtained with coal and wood fuel depend to some extent upon the chemical and physical character of the limestone. A high-silica or high-alumina stone requires more coal. But since a high chemical purity is required, these so-called " bastard " limes are seldom burned. A high-alumina stone has a tendency to produce a hydraulic cement when it slakes, so this class of stone is seldom used.

Coal requirements per ton of stone are one to three in the less efficient kilns. Highly efficient plants with mechanically-controlled draught sometimes report that one ton of coal calcines five tons of stone. The following figures were taken from a very average operation. Stone of average 90 per cent. calcium carbonate, which weighed 110 lb. per cu. ft., was used : 2,000 lb. of coal calcined 6,000 lb. of stone ; 6,000 lb. of stone produced 3,540 lb. of quicklime ; 3,540 lb. of quicklime produced 4,660 lb. of comparatively dry hydrate. This ratio was 1 ton of coal to 1.77 tons of quicklime, and 1 ton of coal to 2.33 tons of hydrate.

A sample of the hydrate when exposed to excess moisture was found to absorb 12 per cent. of its own weight in additional water. This hydrate was considered to be completely slaked before being exposed to the excess moisture, and this opinion was verified by the fact that volume did not increase after the excess moisture was encountered. Affinity for excess moisture indicated that the lime was overburned.

To a small degree, the chemical analysis of the coal affects the efficiency of burning. The coal used in the above case had a fixed carbon content of 55·4 per cent. and a content of 36·1 per cent. volatile matter. The complete analysis of the coal used is :

Moisture	1·13 per cent.
Volatile	36·10 ,,
Fixed carbon	55·40 ,,
Phosphorus	0·015 ,,
Ash	7·38 ,,
Sulphur	2·61 ,,

The heat value of this coal sample was set at 13,967 B.T.U. per ton. Another sample of the coal showed 14,045 B.T.U. Naturally there would be some variation in efficiency, corresponding to the variation in the B.T.U. heat value of the coal.

Testing Cement Mortars for Contraction.

A paper by H. E. Schwiete and H. Berchem, issued by the German Highway Research Department, describes a research, made in accordance with the specification for concrete roads, dealing with the results of contraction measurements, on 4 cm. by 4 cm. by 16 cm. briquettes of cement and sand of mixed grading, with a water-cement ratio of 0.6, in conjunction with the results of tests for contraction measured during the past two years in the Kaiser Wilhelm Institute for Silicate Research.

It is stated that cements with the same contraction values after 28, 56, 90, and 180 days can vary a great deal in their evaporation, while there may be considerable differences in the loss of weight of test pieces which have the same contraction values. Contraction is not a complete indication of the behaviour of cement mortar when drying out, because the relation of evaporation to contraction varies. The water in the larger pores, which dries out first, changes the length less than that which is given off from the mortar when the relative humidity is less. The relation of contraction to evaporation is therefore less between 7 and 14 days than between 14 and 28 days. The relation of contraction to evaporation between 14 and 28 days is practically the same as between 28 to 56 days. Evaporation between 56 and 90 days and between 90 and 180 days is less than between 28 and 56 days.

There is a great deal of variation in the quantity of water given off from the test samples during the first seven days curing and between 7 and 14 days. The difference in evaporation after 14 days was due to the different degrees of combination of water and cement during the first seven days curing. For example, two cements with the least evaporation were rapid hardening cements.

Effect of the Length of the Curing Period.

Samples of coarsely and finely ground Portland cement were tested (1) after 5 days curing at 7 days old, (2) after 26 days curing at 28 days old, and (3) after 26 days curing in water followed by 322 days in trays over water, after which the samples were dried out over sulphuric acid of 1·33 gravity.

The tensile strengths in bending and the compressive strengths of the cements were tested and the values of the contraction/evaporation ratio for 0 to 21 days and 21 to 49 days curing in trays were noted. The cements left residues of 14·9 per cent. and 6·2 per cent. on a sieve with 4,900 meshes to the sq. cm. and 28·4 per cent. and 17·3 per cent. on a sieve with 10,000 meshes to the sq. cm.

Contraction was found to be reduced by longer moist curing before drying out. Thus, after drying out for 83 days in the tray, the briquettes showed the following contractions:

(*a*) Coarsely ground cement :

(1) After 7 days moist curing .. 1·07 mm. per m.
(2) „ 28 „ „ „ .. 1·03 „ „
(3) „ 350 „ „ „ .. 0·8 „ „

(*b*) Finely ground cement :

(1) After 7 days moist curing .. 1·19 mm. per m.
(2) „ 28 „ „ „ .. 1·14 „ „
(3) „ 350 „ „ „ .. 1·01 „ „

Evaporation also drops sharply as the length of moist curing increases. Thus with coarse cement the loss of weight after 28 days moist curing averages 6·5 g. and after 350 days 11.3 g. ; with finely ground cement the loss is 4·1 g. after 28 days and 10·7 g. less after 350 days moist curing than after 7 days. The smaller evaporation is due to the fact that with longer moist curing the proportion of hydrated cement in the mortar increases, while that of uncombined water decreases. The finer grading effects an additional increase in the proportion of hydrated cement and thereby a reduction in evaporation.

When kept in water the strengths also rose with increasing age of the test samples and with the larger amount of combined water. Curves plotted with the contractions as ordinates and the evaporation as abscissæ showed that the longer the period of moist curing the more consistently horizontal is the curve. After 350 days of moist curing the curve for finely ground Portland cement is practically horizontal between 0 and 83 days.

As hydration increases the contraction/evaporation value of the cement rises between 0 and 21 days curing in trays, whereas between 21 days and 29 days this value is greater after 28 days moist curing. After 350 days, however, it is less than after 7 days.

Curves plotted to indicate the influence of length of moist curing show that the contraction of one cement decreased when kept longer in water, whereas a second cement exhibited greater contractions, particularly as the age increased.

Effects of the Drying Agent.

If a less rapid drying agent than saturated solution of potash or sulphuric acid of a gravity of 1·33 is used, the contraction and evaporation are naturally less. Experiments were made to compare the contractions and losses in weight of coarse and fine Portland cement when kept over sulphuric acid of a gravity of 1·244, equivalent to a relative air humidity of 70 per cent., and the results when kept over sulphuric acid of a gravity of 1·33, equivalent to a relative air humidity of 50 per cent. The test samples were previously kept for two days in moist air and then 26 days under water.

Drying out and contraction were found to be not only less, but also more uniform and steady than when the more rapid drying agent, sulphuric acid of 1·33 gravity, is used.

Influence of Fineness.

The fineness of the cement affects the contraction and, particularly, the evaporation. Moreover, the relation of contraction to evaporation also changes with the fineness. The effect of fineness on contraction has therefore been more closely investigated by comparing a number of Portland cements of the same brand but leaving different residues on the 4,900 sieve. While the products from the same works are always subject to certain variations, it may be assumed that over a period of a few months they will vary only slightly in composition, burning and later treatment of clinker, as also in grading and gypsum content.

The contractions were recorded in mm. per m. per 100 g. after 28 and 90 days and the relation of contraction to evaporation between 7 and 28 days, that is for the first 21 days curing in trays. The briquettes were kept partly over sulphuric acid (gravity = 1·33) and partly over saturated solution of potash. During an earlier comparative test with these two drying agents it was found that the contraction over potash solution is about 10 per cent. greater. There is no appreciable change in the contraction/evaporation ratio from 7 to 28 days—from 1·21 to 1·20—so that the results of the contraction measurement for both drying media can be compared. With all the brands tested, contraction decreased with decreasing fineness of grading. The degrees varied, however, for the separate cements.

The evaporation after 28 days shows no clear dependence on the fineness. On the other hand, the relation of contraction to evaporation after 7 to 28 days generally decreases as the fineness becomes less. The relation between fineness of grading and contraction/evaporation at 7 to 28 days is different for the various types of cement.

The contraction/evaporation (7 to 28 days) values permit conclusions to be drawn regarding the reactive capacity of the cement during the past seven days moist curing. Cements with a high contraction/evaporation value would react quickly, and those with a low value slowly.

Table 1 gives the contraction/evaporation values obtained in a test of a cement in which with almost the same remaining content of tricalcium silicate the clay modulus was changed, and the clinker burnt once with, and once without, ½ per cent. fluor spar. The high clay modulus was 2·48 when burnt without and 2·25 when burnt with fluor spar; the lower clay modulus was 1·59 without and 1·60 with fluor spar. As the clay modulus decreases both the contraction and the contraction/evaporation ratio become smaller.

The contraction values were less affected by the fineness of grinding than the contraction/evaporation values. Whereas, for example, the residue of cements Nos. 211 and 212 on the 4,900-mesh sieve dropped from 9·9 to 3·0 per cent., contraction after 28 days had only risen from 0·63 to 0·64 mm.; the contraction/evaporation ratio for 7 to 28 days, however, rose from 2·27 to 2·60 mm./m./100 g. The slow drying out of the mortar made with the more finely ground cement between 7 days and 28 days is doubtless due to the fact that with this cement the mortar test piece is more compact than with the coarsely ground cement.

TABLE I.

No.		Residue on 4,900-mesh sieve (per cent.)	Contraction.		Evaporation after 28 days (g.).	Contraction/evaporation in mm./m./100 g. at 7 to 28 days.
			28 days.	90 days.		
205	Higher clay modulus without CaF_2.	10·0	0·71	1·05	23·8	2·98
206		2·4	0·78	1·20	25·3	3·08
207	Higher clay modulus with CaF_2.	9·5	0·79	1·12	26·7	2·96
208		2·3	0·81	1·24	23·8	3·40
211	Lower clay modulus without CaF_2.	9·9	0·63	0·90	27·8	2·27
212		3·0	0·64	0·94	24·6	2·60
214	Lower clay modulus with CaF_2.	8·5	0·64	0·90	25·7	2·49
215		2·6	0·74	1·08	25·9	2·86

It is noted also that the cements with the high clay modulus of 2·48 and 2·25, which harden more quickly than those with a lower clay modulus of 1·59 and 1·60, have the larger contraction/evaporation values. The bending strengths of cement No. 205, for example, with the clay modulus of 2·48, amount to 36 kg. per sq. cm. compared with 24 kg. per sq. cm. for cement No. 211 having a clay modulus of 1·59.

Effect of Alteration of Water Content.

The test procedure was altered and mortars made with a Portland cement and an iron-Portland cement were gauged with 10, 12, 14, 16 and 18 per cent. of water instead of 15 per cent. The water-cement factor was thus altered from 0·40 at 10 per cent. to 0·48, 0·56, 0·64 and 0·72 with 12, 14, 16 and 18 per cent. water, respectively. The actual water content of the hardened mortar does not, however, agree with the gauging water content, as in mixtures with much water a part is expelled during the time which elapses between gauging and finishing the briquettes. The quantity of water expelled depends on the water-cement factor, the grading of the sand, and on the brand of cement.

Contractions after 28, 56, and 90 days altered only slightly and irregularly with the alteration of the water content. The evaporation, on the other hand, increased as the content of gauging water rose, so that the contraction/evaporation (7 to 28 days) values decreased accordingly. The alteration of the quantity of gauging water thus caused only a uniform alteration of evaporation when drying out.

Conclusions.

Evaporation from the briquettes must be considered when judging the results of contraction tests, and may be recorded in terms of the proportion of contraction to evaporation.

(1) The length of the moist-curing period influences contraction, evaporation, and the contraction/evaporation value. With longer moist curing contraction

and evaporation decrease; the contraction/evaporation values, on the contrary, increase for the first 21 days of curing in trays. An exception, however, was observed in contraction.

(2) Over 70 per cent. relative air-humidity of suitable sulphuric acid (gravity = 1·244), drying out and contraction are more uniform with lower values than over 50 per cent. relative air-humidity of sulphuric acid (gravity = 1·33).

(3) A table of contraction/evaporation values for 7 to 28 days, shown as varying with the fineness and as percentage residue on a 4,900-mesh sieve, gives a definite specific relationship for each different kind of cement. This method of stating the results differentiates the cements better and permits of conclusions on the reactive capacity during the preceding 7 days' moist curing.

(4) Tests in which the gauging water content was altered in mortars made with a Portland cement and an iron-Portland cement led only to a uniform alteration in evaporation when drying out.

In mixtures rich in water the actual water content in hardened mortar does not agree with the gauging water content of the mortar, as during the time between gauging and finishing the briquettes the mortar expels water.

Determination of the Constitution of Portland Cement Clinker by the Metallographic Method

BY TARO TANAKA AND RYUICHI NAITO
(ONODA CEMENT CO. LTD., JAPAN)

MINERALOGICAL examination has been freely used in studying the constituents of cement clinker, but has the disadvantage that minute constituents cannot be clearly observed since the sections must be made thinner than the size of constituent minerals seen by transmitted light. The method of preparation and examination of specimens commonly used in metallography, that is, polishing a prepared plane surface on the specimen, etching with a suitable reagent, and examining with reflected light, has recently been applied to the observation of minute structures of cement clinker by B. Tavasci[1] and H. Insley[2], who have revived a method which had been generally abandoned for several years. The purpose of this paper is to record the results of the authors' investigation on microscopic studies of clinkers whose chemical compositions deviate to a fairly wide extent, and, more especially, to give the results obtained under reflected light and compare these with similar results in experiments with transmitted light.

Samples and Methods of Preparation

The clinkers used as samples were as follows: (1) well-burnt clinker of normal Portland cement, (2) under-burnt clinker of normal Portland cement,

TABLE 1.—CHEMICAL COMPOSITIONS OF SAMPLES.

No.	1	2	3	4	5	6	7
Samples	Well-burnt Clinker	Under-burnt Clinker	"Low-heat" Clinker	"High-iron-oxide" Clinker	High-magnesia Clinker No. 1	High-magnesia Clinker No. 2	White Portland Cement Clinker
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Loss on Ignition	0·34	0·40	0·21	0·89	0.65	0·37	0·52
SiO_2	23·31	23·69	26·18	23·02	24·78	25·10	25·92
Al_2O_3	4·89	4·85	4·25	4·83	5·76	5·67	5·32
Fe_2O_3	3·26	3·24	3·65	4·09	3·42	3·57	0·29
CaO	66·64	66·36	63·81	65·28	57·25	53·49	66·04
MgO	1·28	1·26	1·10	1·31	7·74	11·62	1·25
Insoluble residue	0·11	0·15	0·10	0·05	0·15	0·17	0·20
Free CaO	0·10	1·80	0·26	1·53	0	0	1·60
$4CaO, Al_2O_3, Fe_2O_3$	9·9	9·8	11·1	12·4	10·4	10·9	0·9
$3CaO, Al_2O_3$	7·4	7·1	5·0	5·9	9·5	9·0	13·6
$3CaO, SiO_2$	56·9	47·1	27·6	46·8	2·1	—	30·4
$2CaO, SiO_2$	23·7	32·0	54·0	30·8	69·1	—	50·9

Compound compositions were calculated by Bogue's method.

(1) B. Tavasci, Tonind.-Ztg. (1937) 61; 487u. 502.

(2) H. Insley, Journ. of Research of National Bureau of Standards. (1936) 17; 353.

(3) low-heat cement clinker, (4) high-iron-oxide cement clinker, (5) high-magnesia cement clinker, and (6) white Portland cement clinker. Their chemical compositions are shown in *Table* 1.

The method of preparation and examination was essentially as follows. A flat face is first ground on the clinker specimen with coarse silicon carbide, and the final grinding is done with fine emery. After careful washing the specimen is polished with a mixture of chromium oxide and ethyl alcohol on a rotary lap covered with coarse duck. The specimen is then etched with a suitable reagent, and is examined with a vertical illuminator using a plane glass reflector, pale bluish filter, and an attached source of light. *Table* 2 shows the reagents and etching methods used in the investigation.

TABLE 2.—ETCHING REAGENTS AND ETCHING PROCESS.

No.	Etching Reagents	Etching Method	
		Temperature	Time (seconds)
1	HNO_3 1 c.c. + C_2H_5OH 100 c.c.	Room temperature	3
2	N-$H_2C_2O_4$ 10 c.c. + C_2HO_3H 90 c.c.	do.	5 to 10
3	HF(40%) 10 c.c. + H_2O 100 c.c.	do.	3
4	H_2O	do.	10

Results of Observations by Reflected Light

In well-burnt Portland cement clinker, Alit occurs abundantly and usually in well-defined crystals of hexagonal forms ; it is easily identified by its hexagonal or prismatic crystals. *Fig.* 1, a photomicrograph with reflected light, shows Alit in hexagonal forms, Belit with fine intricate striations, and a ground mass which exhibits higher reflectivity than any other parts. *Fig.* 2 shows another type of Belit observed in well-burnt clinker. This type of Belit is also observed when well-burnt clinker is reheated at 1,375 deg. C. for half an hour and then cooled to 1,000 deg. C. When well-burnt clinker is cooled rapidly in cold air, however, this type of Belit is absent.

In under-burnt Portland cement clinker Alit is observed in comparatively small amounts and Belit predominates ; it is easily recognised by its complicated striations, somewhat long in the shape, but the individual boundaries of crystals are not sharply distinguished. *Fig.* 3 shows the complicated striations of Belit. *Figs.* 4, 5 and 6 are microphotographs of specimens of low-heat, high-iron-oxide, and high-magnesia (MgO, 7·7 per cent.) clinkers respectively. They show the complicated striations of Belit, which seem to be relatively long and thick. *Fig.* 7 shows high-magnesia (MgO, 11·6 per cent.) clinker. In this micro-photograph the small crystals (marked M in *Fig.* 6) predominate in brown or brownish black colours and when observed under a polarising microscope they show very high birefringence in thin sections.

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Fig. 1.

×710

Fig. 2.

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Fig. 3.

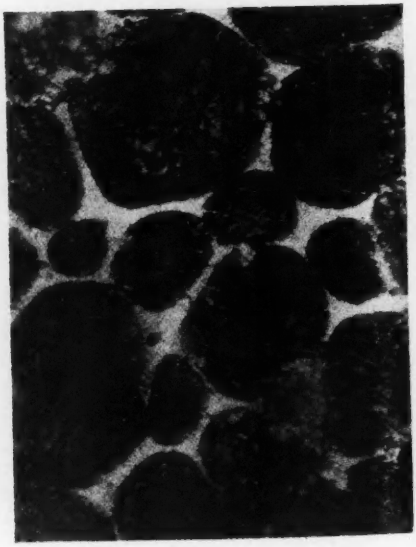

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Fig. 4.

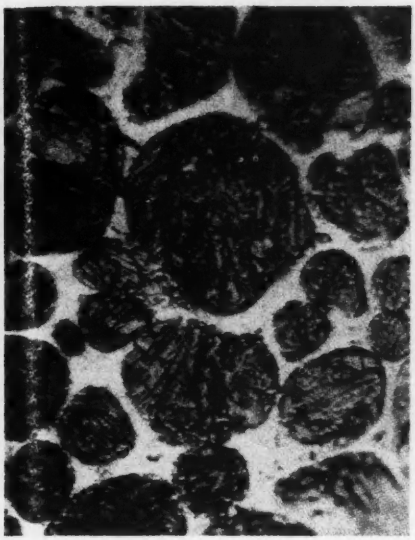

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Fig. 5.

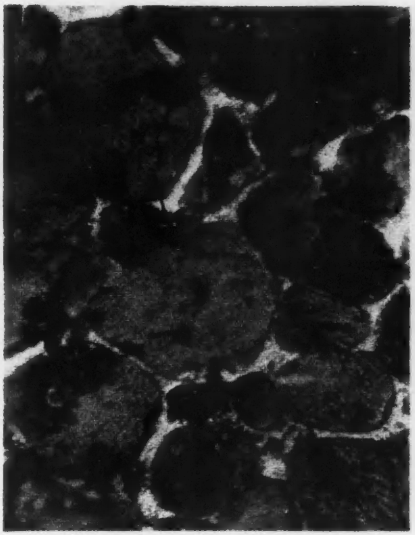

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Fig. 6.

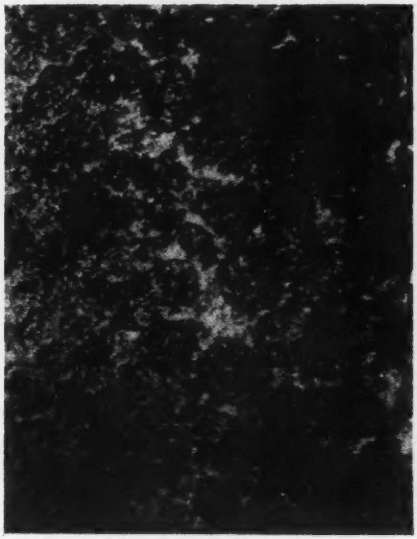

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Fig. 7.

The white Portland cement clinker contains a large amount of small masses of white Belit, which shows fine striations with reflected light; in the ground mass the isotropic body predominates in thin sections.

As a result of these investigations the conclusion was reached that the metallographic method using polished and etched specimens, when combined with the petrographic method, aids considerably in studying the composition of clinker.

Recent Patent Relating to Cement.

Portland Cement.

491,921. L. P. Basset. March 9, 1937.

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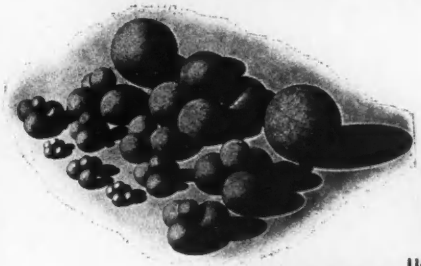

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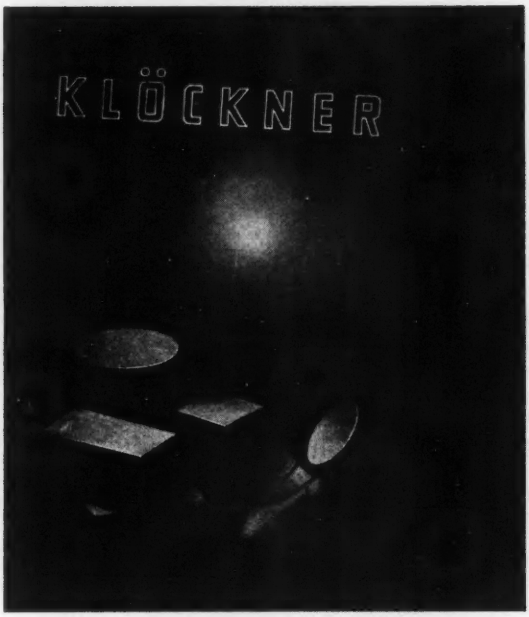

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